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# NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

No. 1163

THE SYNTHESIS AND PURIFICATION OF AROMATIC HYDROCARBONS

IV - 1,2,3-TRIMETHYLBENZENE

By J. M. Lamberti, T. W. Reynolds, and H. H. Chanan

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SUMMARY

A 6-gallon quantity of 1,2,3-trimethylbenzene was prepared and purified in a four-step synthesis involving the condensation of 1,3-pentadiene with crotonaldehyde. The dimethylcyclohexenecarboxaldehydes formed were hydrogenated to give the corresponding isomeric dimethylcyclohexylcarbinols. The dehydration of the carbinols and the subsequent dehydrogenation of the trimethylcyclohexenes yielded the 1,2,3-trimethylbenzene. The over-all yield was 24 percent; the physical properties of the material are given.

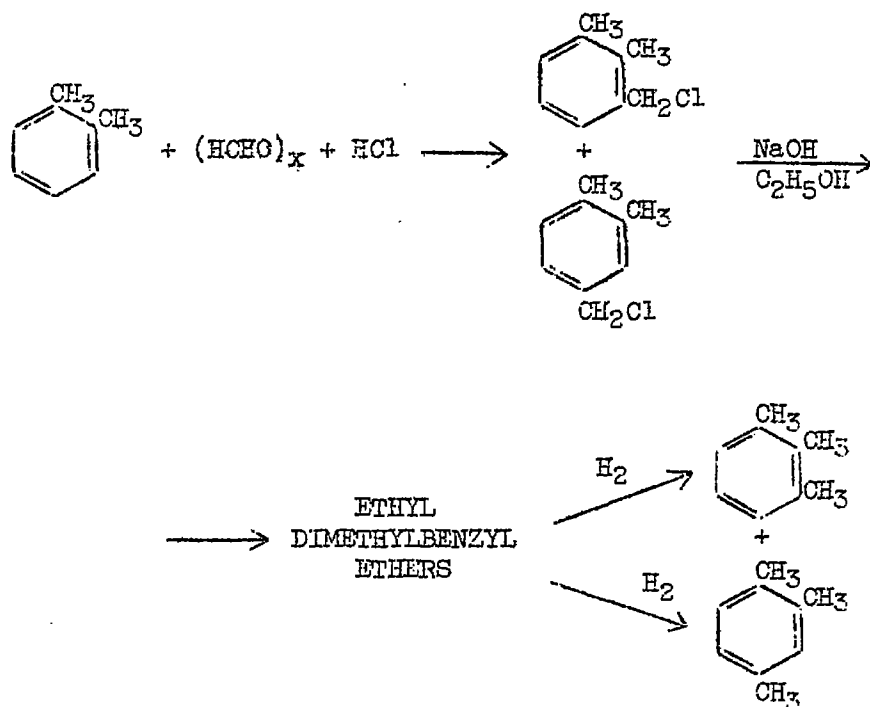
INTRODUCTION

The preparation of pure 1,2,3-trimethylbenzene was undertaken as a part of the program being conducted at the NACA Cleveland laboratory on the study of aromatic hydrocarbons as possible components of aviation fuel. The methods of synthesis of other aromatic hydrocarbons prepared at this laboratory are given in references 1 to 3. Several methods of preparing 1,2,3-trimethylbenzene that are reported in the literature were considered not suitable for practicable large-scale synthesis.

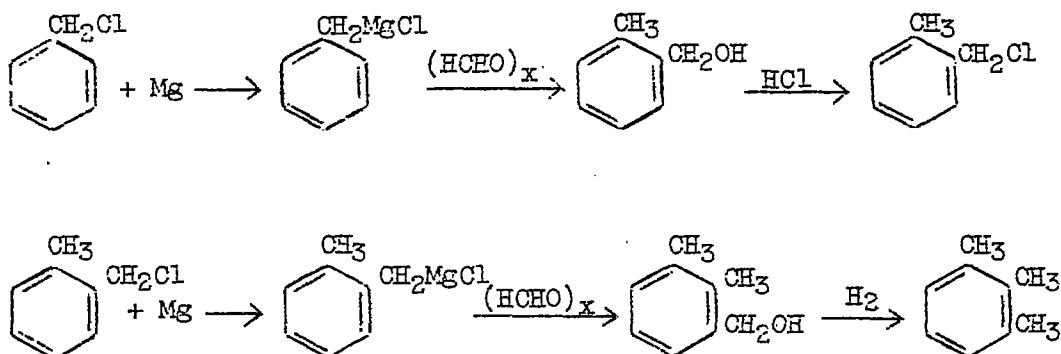
The hydrocarbon was first prepared in 1886 by Jacobson (reference 4) by the decarboxylation of 3,4,5-trimethylbenzoic acid. In 1887 Jacobson and Deike (reference 5) prepared the hydrocarbon by the treatment of 1,3-dimethyl-2-bromobenzene with methyl iodide and sodium. In 1919 von Auwers (reference 6) synthesized the compound by treating 1,2-dimethyl-3-iodobenzene with methyl iodide and sodium.

The preparation of hemimellitene by the chloromethylation of o-xylene, using the method of von Braun and Nelles (reference 7), produced a mixture of 1,2,4- and 1,2,3-trimethylbenzenes. Preliminary

investigations of this method at the Cleveland laboratory showed an over-all yield of 10 percent of the 1,2,3-trimethylbenzene and 30 percent of the 1,2,4-isomer, which did not justify large-scale synthesis. The reactions are as follows:



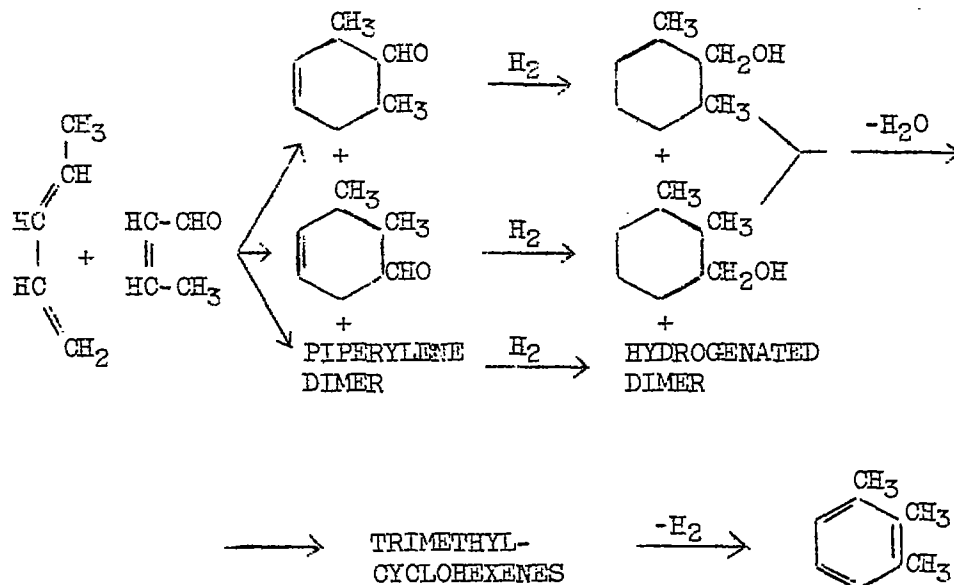
In a series of Grignard reactions starting with benzyl chloride and subsequent reactions based on the Tiffeneau rearrangement Smith and Spillane (reference 8), who based their work partly on the investigations of P. O. Tawney and C. L. Agre conducted at the University of Minnesota from 1934-1936, were able to increase the over-all yield of hemimellitene from 11 percent, as obtained by Agre, to 26 percent. The method described in reference 8 was investigated rather extensively but, on account of the considerable amount of time involved in the large-scale Grignard reactions and the difficulty of the purification of the various intermediates, it did not warrant further large-scale runs. The reactions are as follows:



The method that proved successful was the Diels-Alder condensation as reported by Joshel and Butz (reference 9). The adaptation of this method to the preparation of aromatic hydrocarbons was reported by Tom and Boord at a meeting of the American Chemical Society at Cleveland, Ohio, in April 1944 (reference 10).

## DISCUSSION OF SYNTHESIS

The synthesis of 1,2,3-trimethylbenzene was carried out in 24-percent over-all yield by the following procedure:



Piperylene (1,3-pentadiene) and crotonaldehyde were condensed in an autoclave at 200° C for 4 hours. When 30 to 40 percent (by weight) of the crotonaldehyde was used, the yields of the mixture of the dimethylcyclohexenecarboxaldehydes were 40 to 55 percent. The pressures developed in the autoclave were 300 to 400 pounds per square inch and the pressure dropped to about 250 pounds per square inch at the completion of the condensation. When 40 to 50 percent (by weight) of the crotonaldehyde was used, however, the yields were considerably lower (25 to 30 percent) and unusually high pressures, 500 to 1670 pounds per square inch (fig. 1), developed. No explanation can be offered for the occurrence of the unusually high pressures because the temperature remained at 200° C within  $\pm 5^\circ$ . When piperylene alone was added to the autoclave and heated to 200° C for periods of time up to 3 hours no unusual pressures developed.

The reaction mixture was stripped of its low and high boiling components. The adduct, boiling from 170° to 190° C at atmospheric pressure (approximately 120° C at 50 mm), was approximately 55 percent of the theoretical yield based on the amount of crotonaldehyde used. Both the piperylene and crotonaldehyde were used as commercially obtained without further purification. The commercial piperylene was 80 percent pure, and according to Craig (reference 11) only the trans-isomer reacts in the diene condensations.

The adduct, a mixture of dimethylcyclohexenecarboxaldehydes, was hydrogenated to the corresponding dimethylcyclohexylcarbinols in an autoclave using a nickel hydrogenation catalyst at a temperature of 120° C. The hydrogenation proceeded readily at 120° C, but the temperature was always raised to 150° C at the end to insure complete hydrogenation.

The mixture of the carbinols was taken from the autoclave without purification and dehydrated by passing the material through a 2-inch by 10-foot column packed with alumina, which was heated to between 390° and 400° C. The resulting crude trimethylcyclohexene mixture, which was obtained in approximately 92-percent yield, was carefully fractionated through a 2-inch by 12-foot column containing Fenske-type packing and yielded 63 percent of the charge as pure trimethylcyclohexenes. Careful fractionation (100-theoretical plate column, 50:1 reflux ratio) was necessary to remove the piperylene dimer because the dimer boiled at approximately the same temperature as the final hydrocarbon.

The purified trimethylcyclohexenes were dehydrogenated by passing the material through a 2-inch by 10-foot column containing chromia-alumina catalyst heated to a temperature between 450° and 470° C.

The 1,2,3-trimethylbenzene, which was obtained in 79-percent yield from the dehydrogenation of the purified trimethylcyclohexenes, was purified by fractional distillation in a 100-plate column. The final product had a yellow color after fractionation and it was necessary to reflux the material over sodium to obtain a colorless material. The over-all yield of 1,2,3-trimethylbenzene in the synthesis was approximately 24 percent.

The physical constants of the "best" sample obtained at this laboratory and of the "engine grade" sample material are shown in table I along with values obtained at other laboratories (references 8, 12, and 13) for comparison. Freezing curves of the best sample are shown in figure 2(a) and of the engine grade sample in figure 2(b). Readings as shown in the curve were taken on a platinum resistance thermometer in ohms and converted (by computation) to Centigrade degrees.

#### EXPERIMENTAL DETAILS

A 6-gallon quantity of pure 1,2,3-trimethylbenzene was prepared according to the foregoing procedure. Typical quantities of reactants and yields in the various steps are presented as follows.

Condensation of crotonaldehyde and piperylene. - In one run 5.57 kilograms (81.8 moles) of commercial piperylene and 4.54 kilograms (64.9 moles) of commercial crotonaldehyde were added to a 20-liter rocking autoclave equipped with thermostatically controlled electric heaters and a jacket for air cooling. The temperature was held at 200° C and the reaction allowed to proceed until the pressure dropped to a constant value, usually 250 pounds per square inch. The condensation required about 5 hours. The condensation product after stripping yielded 4.83 kilograms (54 percent) of material boiling from 170° to 190° C. No attempt was made to separate the piperylene dimer from the dimethylcyclohexencarboxaldehydes because the separation could be accomplished sharply and more easily in a later step.

An attempt to separate the possible isomeric aldehydes by fractionation in a 1-inch by 7-foot glass column, packed with 1/4-inch single turn glass helices, tested efficiency 82 plates, proved unsuccessful.

Hydrogenation of the dimethylcyclohexencarboxaldehydes. - The crude aldehyde mixture, 9.1 kilograms, and nickel hydrogenation catalyst (454 grams) were added to the same autoclave that was used for the condensation runs. The autoclave was heated to 120° C and

the hydrogen was intermittently charged until the pressure no longer dropped, indicating that the hydrogenation was completed. The time required for complete hydrogenation was 10 to 12 hours when fresh catalyst was used. The amount of the reaction product recovered was 9.1 kilograms (97 percent). The same catalyst could be used for several runs but the reaction time was extended.

Distillation of a small portion of the obtained alcohol (fig. 3(a)) showed that the crude mixture was about 70 percent of the desired alcohols, 20 percent of the piperylene dimer, and 10 percent low-boiling material. The boiling range of the dimethylcyclohexylcarbinols was 207° to 215° C at atmospheric pressure.

Dehydration of the dimethylcyclohexylcarbinols. - In a typical dehydration run 8.3 kilograms of the crude-alcohol mixture was taken directly from the hydrogenation reaction without further purification and passed through a 2-inch by 10-foot column packed with alumina catalyst. The temperature of the column was maintained between 380° and 400° C; approximately 10 hours was required to complete the dehydration. The recovered reaction product consisted of 6.62 kilograms of the hydrocarbons. The trimethylcyclohexenes were then separated from the other constituents by fractionation in a 2-inch by 12-foot column containing Fenske-type packing. A typical distillation curve of trimethylcyclohexenes is shown in figure 3(b). The main part of the curve shows the cyclohexene isomers; the end of the curve shows the separation of the dimer. The yield of the trimethylcyclohexenes (63 percent) approximated the percentage of the alcohol content of the crude material as shown by figure 3(a). This curve indicated that the pure alcohol would probably give nearly quantitative yields upon dehydration.

Dehydrogenation of the trimethylcyclohexenes. - A charge of 19.2 kilograms of the trimethylcyclohexenes (boiling range 146° to 156° C) was passed through a 2-inch by 10-foot column packed with chromia-alumina catalyst. The dehydrogenation, which was maintained at a temperature between 450° and 470° C, required about 65 hours.

The dehydrogenated material (17.3 kg) was fractionated on a 100-theoretical-plate column to yield 14.72 kilograms (79 percent) of 1,2,3-trimethylbenzene (fig. 3(c)). It was necessary to strip the product over sodium in order to remove the yellow color.

Aircraft Engine Research Laboratory,  
National Advisory Committee for Aeronautics,  
Cleveland, Ohio, May 2, 1946.

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TABLE I - PHYSICAL CONSTANTS OF 1,2,3-TRIMETHYLBENZENE

Source	Freezing point (°C)	Boiling point at 760 mm (°C)	Index of refraction $n_D^{20}$	Density at 20° C (grams/ml)
Reference 8	-25.41	-----	1.5130	0.8944
Reference 12	-25.47	176.10	-----	.8951
Reference 13	-25.450	176.15	1.5139	.8950
NACA "best" sample	-25.41	176.09	1.5138	.8944
NACA engine sample	-25.97	176.05	1.5137	.8943

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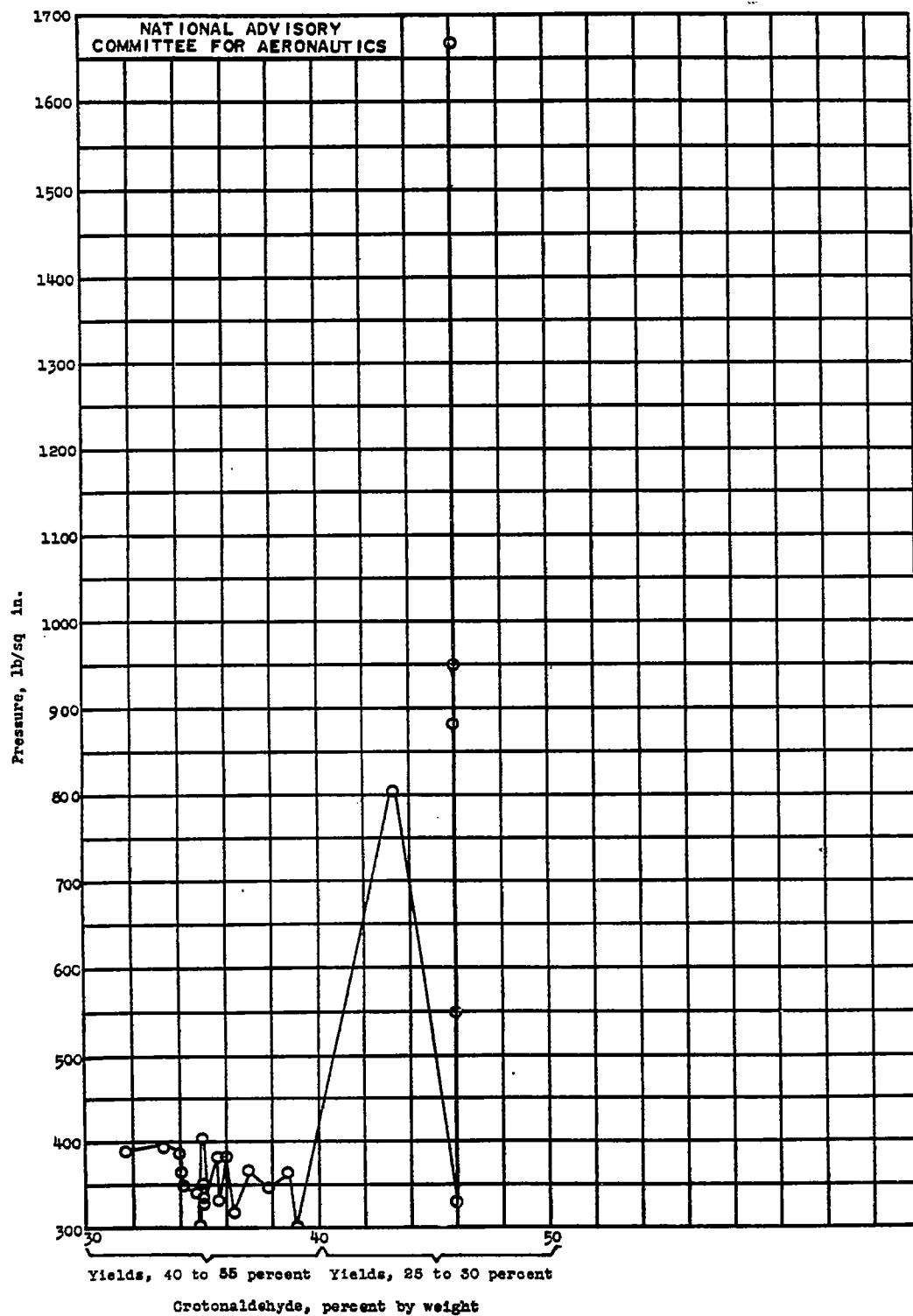


Figure 1. - Variation of pressure in autoclave with weight of crotonaldehyde used and yields obtained of dimethylcyclohexenecarboxaldehydes.

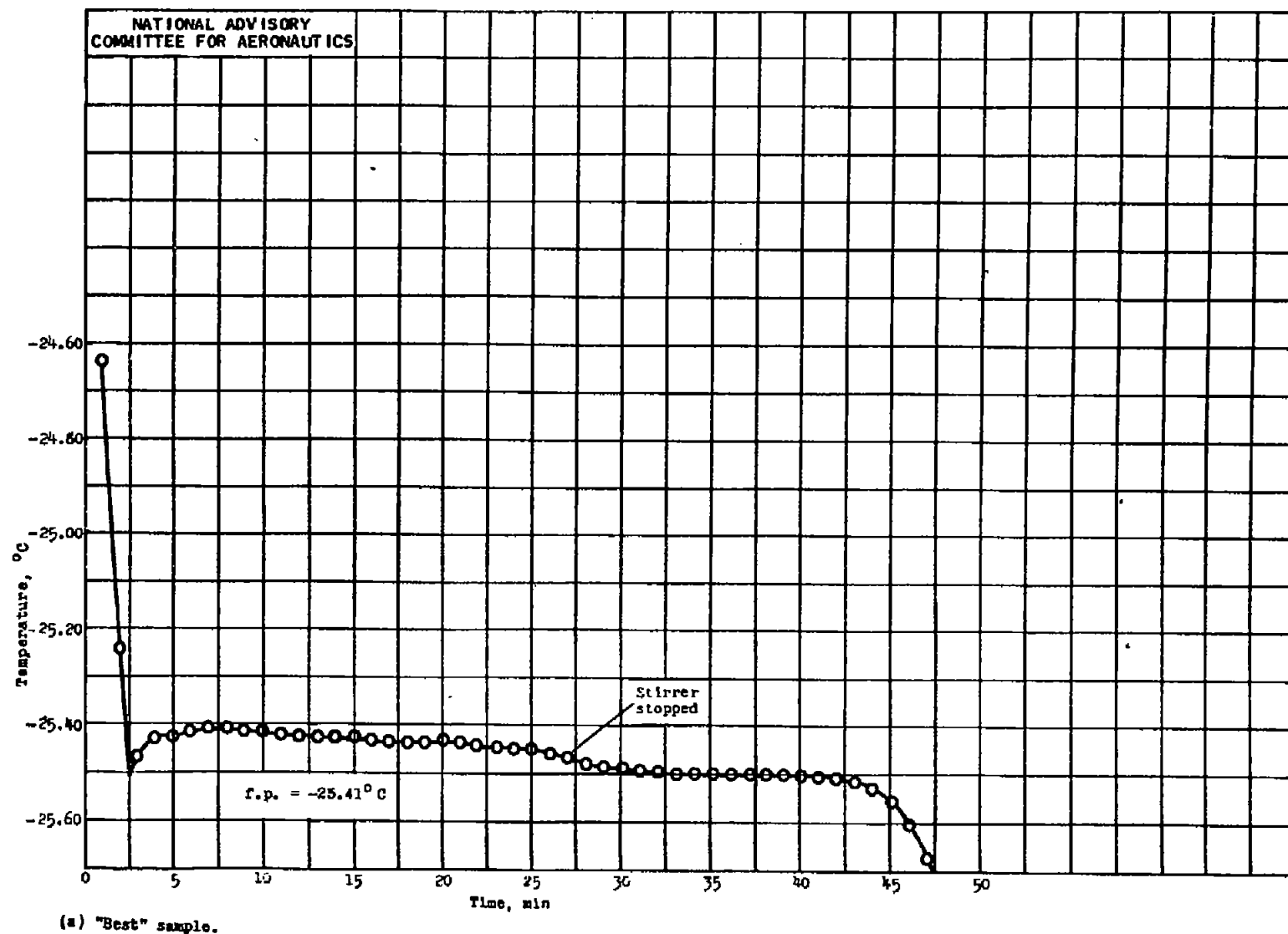
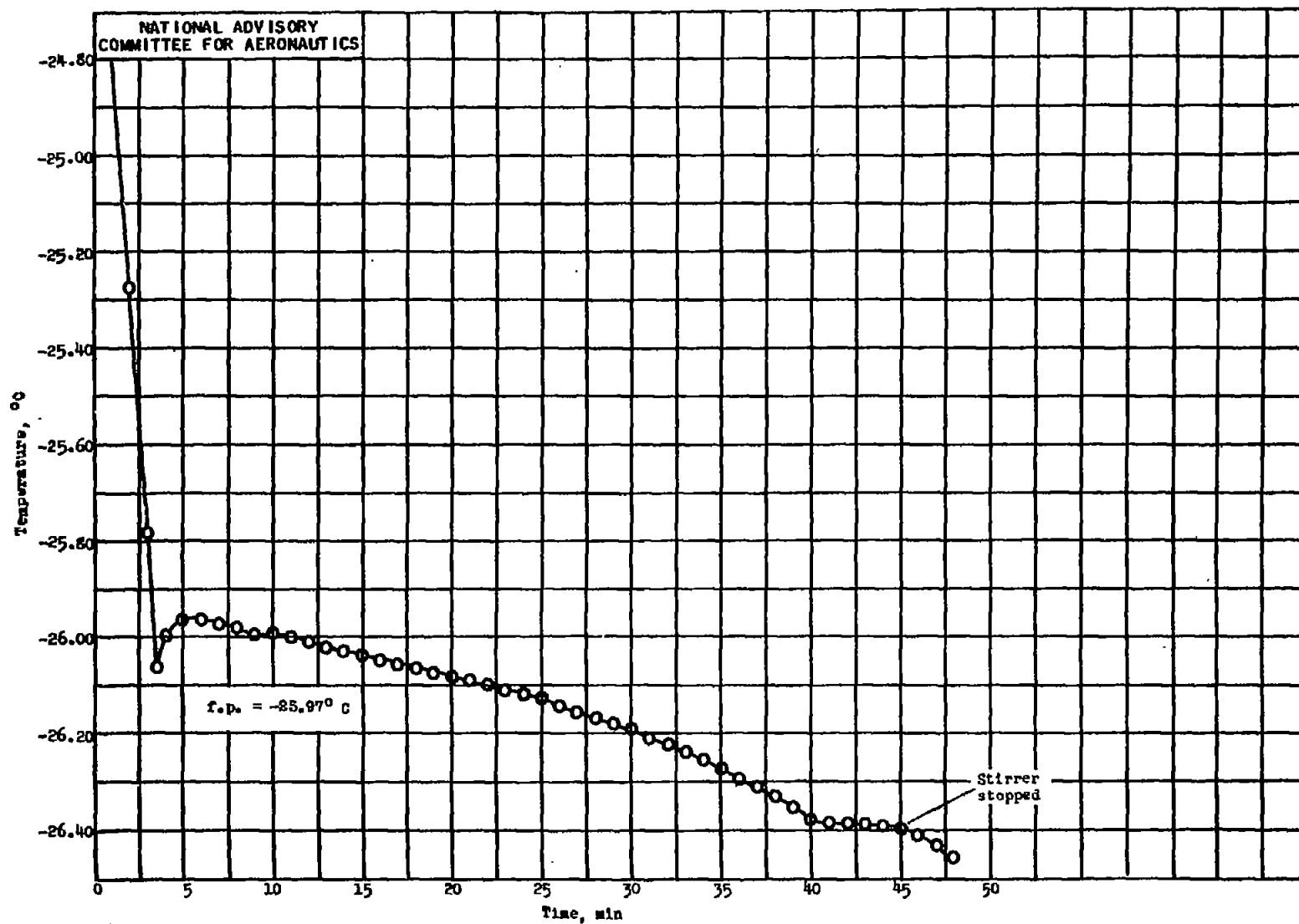
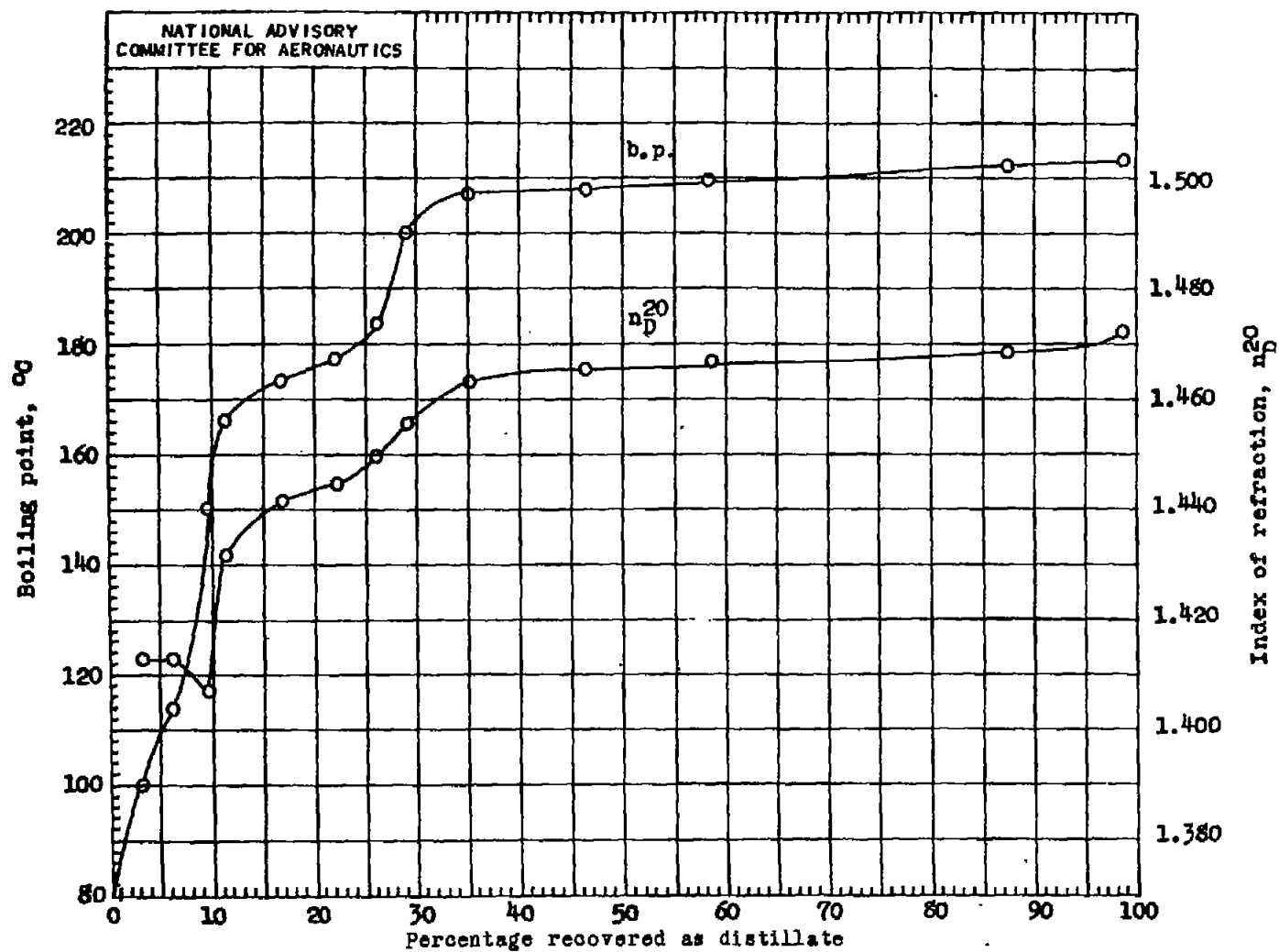


Figure 2. - Time-temperature freezing curves of 1,2,3-trimethylbenzene.



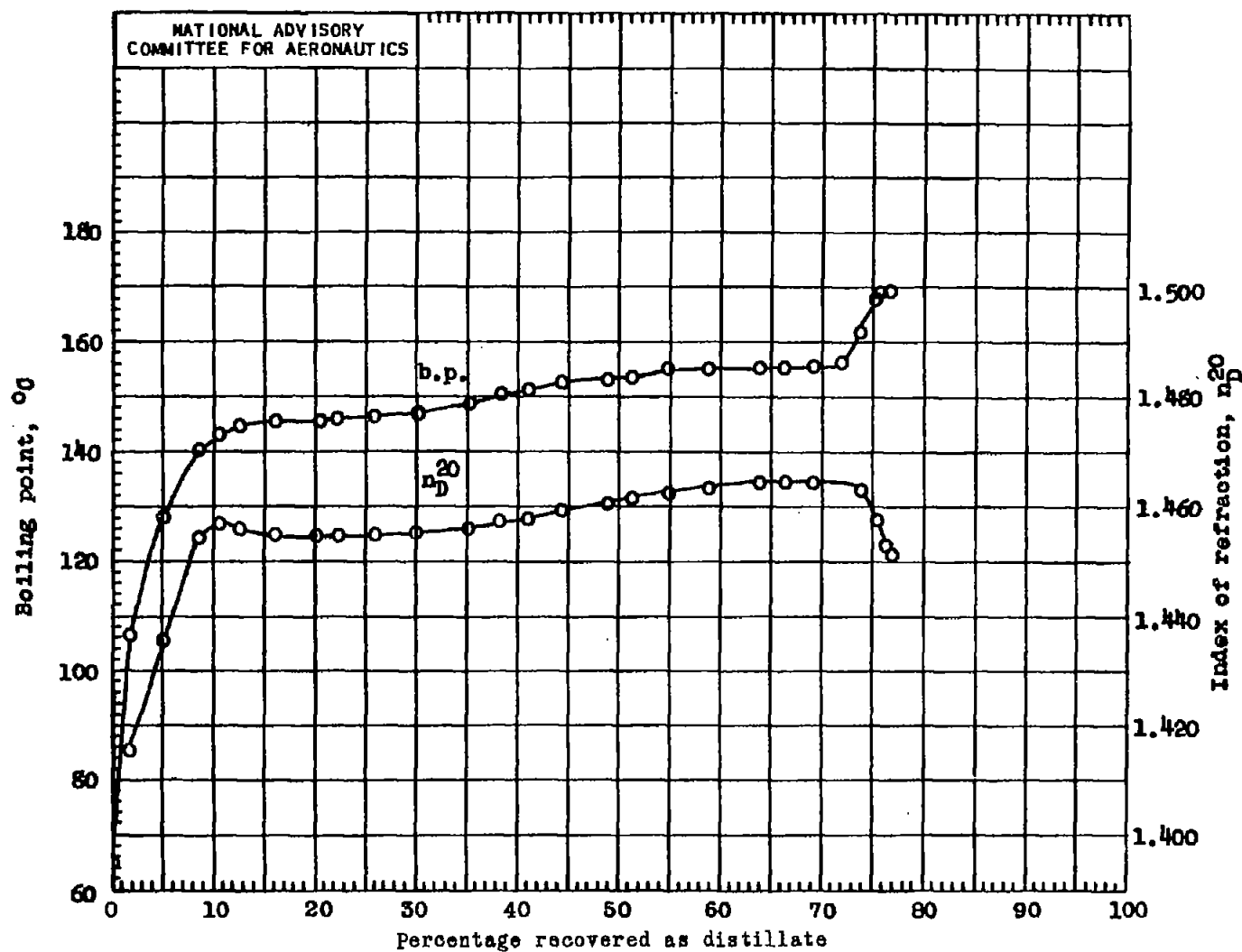
(b) Engine grade sample.

Figure 2. - Concluded. Time-temperature freezing curve of 1,2,3-trimethylbenzene.



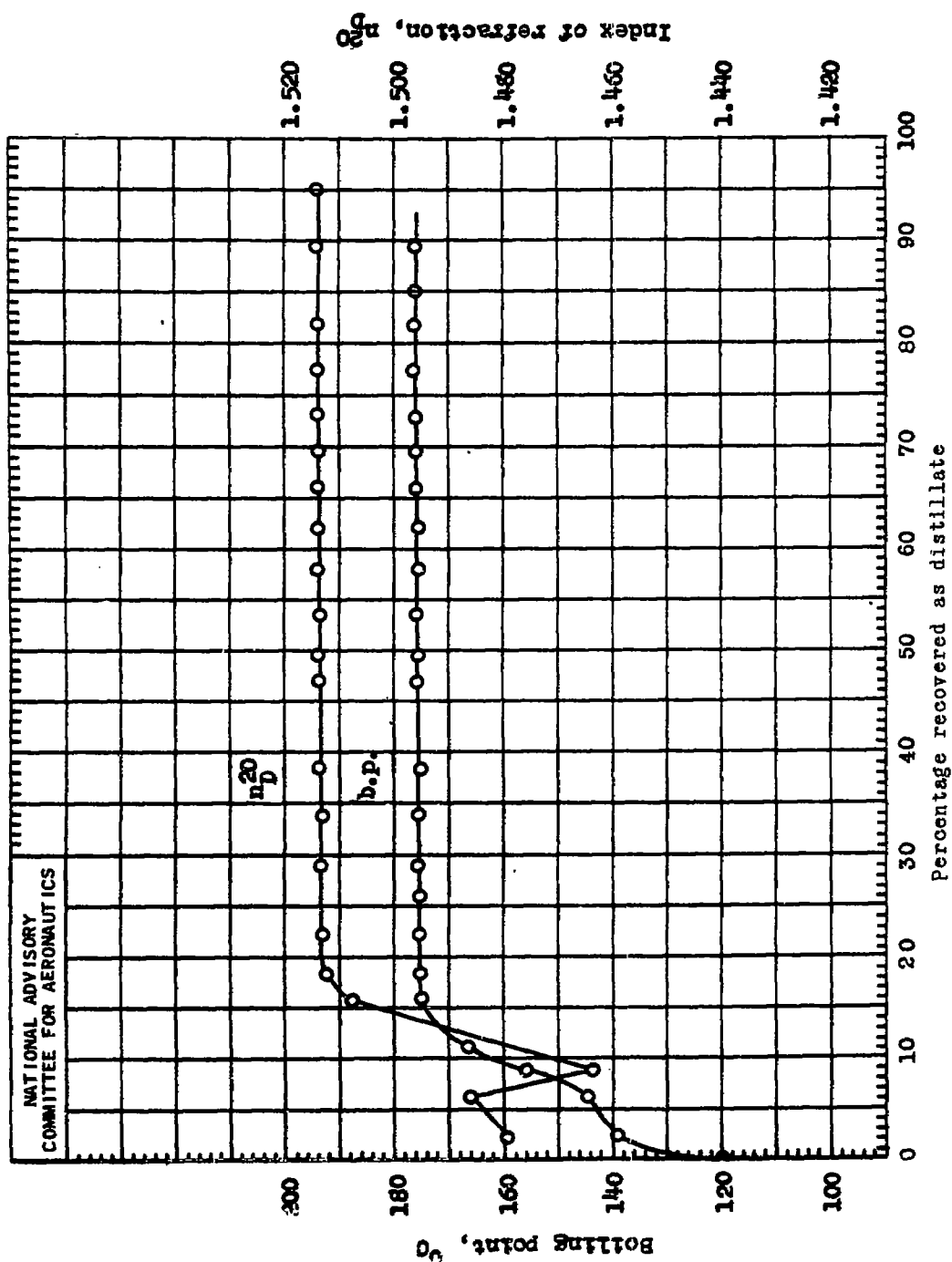
(a) Dimethylcyclohexylcarbinols.

Figure 3. - Variation of boiling point and index of defraction with percentages recovered as distillate.



(b) Trimethylcyclohexenes.

Figure 3. - Continued. Variation of boiling point and index of defraction with percentages recovered as distillate.



(c) 1,2,3-Trimethylbenzene.

Figure 3. - Concluded. Variation of boiling point and index of refraction with percentages recovered as distillate.